(1)

YEARLY SUMMARY OF RESEARCH PERFORMED UNDER OFFICE OF NAVAL RESEARCH, MECHANICS DIVISION

"NOVEL METALLACARBORANES AND THEIR DERIVATIVES"

BY

Professor M. Frederick Hawthorne

Period Covered: October 1, 1990 - July 31, 1991

Organization: University of California, Los Angeles

Organization Address: Department of Chemistry and Biochemistry
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a) Description of the Scientific Research Goals:

This project entails chemical studies directed at the synthesis of functionalized iron (II)-containing metallacarborane compounds which may serve as highly energetic burn-rate modifiers (BRM's) in propellant mixtures. When chemically attached to polymeric binders via suitable functional groups, these energetic materials may offer significant advantages over conventional BRM's. Additional tasks of this project are: (1) to prepare functionalized carborane derivatives for supply to other laboratories for evaluation and incorporation into experimental polymeric materials related to energetic materials applications as well as (2) exploring new and novel chemistry associated with these systems.

b) Significant Results in the Past Year:

We have made considerable progress during the past year. A variety of experiments have been carried out which were directed at probing the chemistry of iron metallacarboranes. As reported in our last progress report, the complex [*closo*-$C_2B_9H_{11}Fe(CO)_2]^{2-}$ (**1**) is quantitatively synthesized by reduction of *closo*-$C_2B_9H_{11}Fe(CO)_3$ (**2**) with two equivalents of sodium napthalide in tetrahydrofuran.

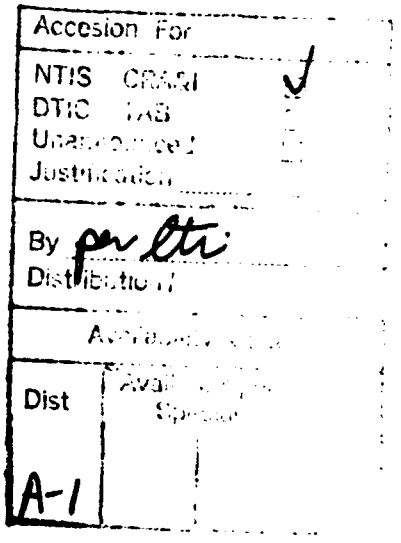
A variety of neutral iron (II) ferracarboranes of the type [*closo*-$C_2B_9H_{11}FeCOLL']$ (L = CO, PPh_3, $P(OCH_3)_3$; L' = CO, PPh_3, CH_3CN, $P(OCH_3)_3$ have been prepared by the Cu(I) oxidation of (**2**) in the presence of the designated monodentate ligands. These compounds have been structurally characterized by single-crystal X-ray diffraction.

Additionally, the precursor (**2**) proved to be a useful synthon for the preparation of (π-arene) metallacarboranes. The photolysis of (**2**) in benzene resulted in the desired complex, *closo*- (η^6-C_6H_6)$FeC_2B_9H_{11}$, in 89% yield. Although this reaction proved quite succesful, all attempts to functionalize either the carborane moiety or the arene moiety to develop charge-compensated comonomers proved unsuccessful. A variety of carborane and metallacarborane compounds were provided to ONR contractors for their evaluation.

Finally, the chemistry which was developed for the iron (II) ferracarboranes proved valuable in the expansion to other metal systems, such as samarium, ytterbium, and thallium metallacarboranes.

c) Plans for Next Year's Research:

None. This past year was the final funding year.



OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
1 October 1990 through 30 September 1991

R & T Number: N00014-85-K-0772 (Contract Number)
4326-808 (Work Unit Number)

Contract/Grant Title: "Novel Metallacarboranes and Their Derivatives"

Scientific Officer: Richard S. Miller

Principal Investigator: Professor M. Frederick Hawthorne

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a) Number of Papers Submitted to Refereed Journal but not yet published: 1

b) Number of Papers Published in Refereed Journals: (List attached): 4

c) Number of Books or Chapters Submitted but not yet Published: 0

d) Number of Books or Chapters Published (List Attached): 0

e) Number of Printed Technical Reports & Non-Refereed Papers (List Attached): 0

f) Number of Patents Filed: 0

g) Number of Patents Granted (List Attached): 0

h) Number of Invited Presentations at Workshops or Professional Society Meeting (List Attached): 0

i) Number of Presentations at Workshops or Professional Society Meetings (List Attached): 0

j) Honors/Awards/Prizes for Contract/Grant Employees: (List Attached, may include Society Awards/Offices, Promotions, Faculty Awards/Offices, etc.) 0

k) Providing the following information will assist with statistical purposes.

PI/CO-PI:	TOTAL	1	Grad Students:*	TOTAL	3
	Female	0		Female	2
	Minority*	0		Minority*	0

Post Doc:**	TOTAL	1
	Female	1
	Minority*	0

l) Degrees Granted (List Attached): 1

* Underrepresented or minority groups include Blacks, Hispanics, and Native Americans. Asians are not considered an underrepresented or minority group in science and engineering.

** Supported at least 25% this year on contract/grant.

LIST OF PUBLICATIONS/REPORTS/PATENTS/GRADUATES

1. Papers Published in Refereed Journals:

a) "Synthesis and Molecular Structure of closo-3-(η^6-C_6H_6)-3,1,2-$FeC_2B_9H_{11}$" Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *J. Organomet. Chem.*, **1990**, *394*, 29.

b) "Synthesis and Structural Characterization of Mononuclear Iron (II) Ferracarboranes" Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics*, **1991**, *10*, 670.

c) "A Ferracarborane Analogue to $[Fp]^-$. Synthesis and Reactions of $[closo\text{-}3,3\text{-}(CO)_2\text{-}3,1,2\text{-}FeC_2B_9H_{11}]^{2-}$" Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics*, **1991**, *10*, 1054.

d) "Metallacarborane Complexes That Incorporate the Lanthanides. Synthesis, Molecular Structure, and Spectroscopic Characterization of Dicarbollide Complexes of Samarium and Ytterbium" Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009.

e) "Dicarbollide Complexes of Thallium: Structural and ^{11}B NMR Studies" Manning, M. J.; Knobler, C. B.; Hawthorne, M. F.; Do, Y. *Inorg. Chem.*, **1991** (accepted).

2. Books (and sections thereof) Published: None.

3. Technical Report, Non-Refereed Papers: None.

4. Presentations: None.

5. Patents Granted: None.

6. Degrees Granted (name, date, degree):

Sharon S. Lee	1990	Doctor of Philosophy

LIST OF AWARDS/HONORS/PRIZES

Name of Person Receiving Award	Recipient's Institution	Name of Award	Sponsor of Award
None			

OTHER SPONSORED RESEARCH

(Include title, sponsor's name, dollar amount and start and end dates for the award)

Other support as of 08/01/91

(a) National Science Foundation, NSF-91-11437; 10% effort
"Synthesis, Reactivity and Catalysis of Novel Metallacarboranes"
Period of Support: 06/01/91 - 05/31/93; Total Annual Costs: 145,000.

(b) National Science Foundation; DMR-90-14487; 5% effort
"Amorphous and Crystalline Ceramic Carbides from Chemical Precursors"
Joint grant with UCLA Material Science Department
Period of Support: 10/01/90 - 09/30/93; Total Annual Costs: $100,000 (for Chemistry).

(c) National Institutes of Health; USPHS CA-31753; 15% effort
"10-Boron Labeled Antibodies for Cancer Therapy"
Period of Support: 07/01/90 - 06/30/93; Total Annual Costs: $366,534 (Includes Subcontract to the City of Hope).

(d) National Institutes of Health; USPHS CA-53870; 5% effort (no salary taken)
"Bifunctional Antibody Mediated Neutron Capture Therapy"
Period of Support: 04/01/91 - 03/31/96; Total Annual Costs: $154,529 (Includes Subcontact to the City of Hope).

(e) U.S. Department of Energy; EG&G C88-101942; 5% effort
"Power Burst Facility/BNCT Program: Melanoma Treatment Evaluation Program." Program Director: Merle L. Griebenow (Idaho National Engineering Laboratory)
Subcontractual P.I.: M. Frederick Hawthorne
Subcontractual Title: "Boronated Liposome Development and Evaluation"
Period of Support: 03/01/91 - 02/28/94; Total Annual Costs: $185,729.

Proposals Pending Review

(a) National Institutes of Health; 1-PO1-CA43904; 10% effort
"Colon Cancer and Engineered Antibodies"; P.I.: John E. Shively, Ph.D. (City of Hope Nat'l Med Ctr)
Subcontractual Title: "Novel Metal Ion Complexes for Diagnosis and Therapy"
Period of Support: 12/01/91 - 11/30/96; Total Annual Costs Requested: $130,940.